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# The removal of hydrogen sulfide from gas streams using an aqueous metal sulfate absorbent

## Part I. The absorption of hydrogen sulfide in metal sulfate solutions

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### Abstract

The desulfurization of gas streams using aqueous iron(II)sulfate ( $\text{Fe(II)SO}_4$ ), zinc sulfate ( $\text{ZnSO}_4$ ) and copper sulfate ( $\text{CuSO}_4$ ) solutions as washing liquor is studied theoretically and experimentally. The desulfurization is accomplished by a precipitation reaction that occurs when sulfide ions and metal ions are brought into contact with each other. A thermodynamic study has been used to determine a theoretical operating window, with respect to the pH of the scrubbing solution, in which the metal sulfate solution can react with hydrogen sulfide ( $\text{H}_2\text{S}$ ), but not with carbon dioxide ( $\text{CO}_2$ ) from the gas or hydroxide ions from the scrubbing solution. When the absorption is carried out in this window the proposed process should be capable of removing  $\text{H}_2\text{S}$  from the gas stream without uptake of  $\text{CO}_2$  or the formation of metal hydroxides. The pH operating window increases in the order of iron, zinc to copper. Experimental verification showed that the proposed process indeed efficiently removes  $\text{H}_2\text{S}$  when an aqueous  $\text{Fe(II)SO}_4$ ,  $\text{ZnSO}_4$  or  $\text{CuSO}_4$  solution is used as absorbent. However, for an efficient desulfurization the lower pH of the experimental pH operating window using the  $\text{Fe(II)SO}_4$  or  $\text{ZnSO}_4$  solution was higher than indicated by thermodynamics. The reason for this must probably be attributed to a reduced precipitation rate at decreasing pH. When a  $\text{CuSO}_4$  solution is used as washing liquor the solution can efficiently remove  $\text{H}_2\text{S}$  over the entire pH range studied (as low as  $\text{pH} = 1.4$ ). In this case only the upper pH boundary of the operating window (that indicates the possible formation of copper hydroxide or copper carbonates) seems to be a relevant limit in practice. The laboratory experiments indicate that the absorption of  $\text{H}_2\text{S}$  in a  $\text{CuSO}_4$  solution, at the experimental conditions tested, is a gas phase mass transfer limited process. This allows a high degree of  $\text{H}_2\text{S}$  removal in a relatively compact contactor. In addition to the lab scale experiments the potential of the new desulfurization process has also been successfully demonstrated for an industrial biogas using a pilot scale packed bed reactor operated with a fresh and regenerated  $\text{CuSO}_4$  solution. This study indicates that the precipitation reaction of metal sulfates with  $\text{H}_2\text{S}$  can be used successfully in a (selective) desulfurization process, and that it can be an attractive alternative to the desulfurization methods currently used.

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**Keywords:** Desulfurization; Metal sulfide; Precipitation reactions

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### 1. Introduction

Many natural and industrial gases contain  $\text{H}_2\text{S}$ . The presence of  $\text{H}_2\text{S}$  usually prohibits the direct use of these gases because of its toxic properties, the formation of  $\text{SO}_2$  upon combustion (acid rain), and the problems it (usually) gives in

downstream processing. This means that it is often necessary to remove  $\text{H}_2\text{S}$  from the gas stream prior to use. If any  $\text{CO}_2$  is present in the gas, simultaneous removal of  $\text{CO}_2$  from the gas stream can occur. This phenomenon generally increases the amount of chemicals required during the removal step, and is therefore not desired. Many processes have been developed to remove  $\text{H}_2\text{S}$  from gas streams, see e.g. Kohl and Nielsen [1]. In case of regenerative processes the reagent used to capture  $\text{H}_2\text{S}$  can be recovered. Selective  $\text{H}_2\text{S}$  removal can be accomplished by using a process based on the precipitation reaction

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### Nomenclature

$a$	specific surface area in the bubble column ( $\text{m}^2 \text{m}^{-3}$ )
$C$	concentration ( $\text{mol m}^{-3}$ )
$h$	height of the liquid in the bubble column (m)
$k$	mass transfer coefficient ( $\text{m s}^{-1}$ )
$K$	equilibrium constant ( $\text{mol m}^{-3}$ , $\text{mol}^2 \text{m}^{-6}$ )
$m$	distribution coefficient
$P$	pressure (Pa)
$T$	temperature (K)
$v$	velocity ( $\text{m s}^{-1}$ )

### Subscripts

a	acid
G	referring to the gas phase
i	interface
in	referring to the gas entering the bubble column
L	referring to the liquid phase
out	referring to the gas leaving the bubble column
sp	solubility product
sup	superficial
w	wetted

of  $\text{H}_2\text{S}$  with metal ions present in an aqueous solution and a subsequent regeneration of the solid metal sulfide formed. For the reaction of e.g. a bivalent metal ion and the sulfide ion the following overall precipitation reaction can take place:



It is possible, with the proper choice of metal ion and process conditions, to remove  $\text{H}_2\text{S}$  without co-absorption of  $\text{CO}_2$ . By separating the produced  $\text{CuS}$  from the spent absorbent, oxidizing it into  $\text{CuO}$ , and then dissolving the obtained  $\text{CuO}$  back in the spent absorption liquid a closed loop (regenerative) process can be obtained, for details about this manner of operation see ter Maat et al. [2]. The proposed process will be most attractive when selective removal of  $\text{H}_2\text{S}$  is required, as will be the case in most gases containing a high level of  $\text{CO}_2$ . An example of such a gas is biogas, a product of anaerobic digestion of organic waste. A typical composition of such a biogas is given in Table 1 [3]. Normally the  $\text{H}_2\text{S}$  specification for the product gas will vary between 4 and 500 ppmv  $\text{H}_2\text{S}$ , depending upon further use. In the past a number of processes have been developed to utilize the precipitation reaction of metal ions with sulfide. So far, the main utilization of this reaction is found in the removal of heavy metal ions from e.g. electroplating waste streams. In these cases the primary interest was the efficient removal of metal ions from the waste stream. In contrast, only a few processes are dedicated to the removal of  $\text{H}_2\text{S}$  from a gas stream using metal ions. An example is the chemsweet process [4], a non-regenerative process that utilizes zinc ions provided by the dissolution of basic

Table 1  
Typical biogas composition

Component	Composition (vol.%)
$\text{CH}_4$	52–95
$\text{CO}_2$	9–45
$\text{H}_2\text{S}$	0.001–2
$\text{H}_2$	0.01–2
$\text{N}_2$	0.1–4
$\text{O}_2$	0.02–6.5
Ar	0.001
CO	0.001–2
$\text{NH}_3$	Trace
Organics	Trace

zinc salts to remove  $\text{H}_2\text{S}$  from sour gases. In this semi-batch process solid zinc salts are dissolved to replenish the washing liquor. Regenerative processes for the removal of  $\text{H}_2\text{S}$  from geothermal steam have been described by Brown and Dyer [5], and in the patents of Spevack [6] and Harvey [7]. These processes utilize copper solutions to remove  $\text{H}_2\text{S}$  from geothermal steam. In the regeneration step copper sulfide is oxidized at elevated temperature and pressure to  $\text{CuSO}_4$  (in the presence of ammonium ions). The product of this type of process is, apart from a cleaned up steam flow, a concentrated stream of ammonium sulfate. The application of this process is rather limited because the process cannot operate in a closed loop manner if substoichiometric amounts of ammonia are present in the gas stream to be cleaned. For other processes mentioned in literature the recovery of the metal ions from the metal sulfide formed is rather cumbersome in the absence of ammonia. Ehnert et al. [8] describe the use of a cupric halogenide to remove  $\text{H}_2\text{S}$  from a gas. Copper was recovered by means of oxidation of the copper sulfide at elevated temperatures. The products were a regenerated copper solution and impure elemental sulfur. Broekhuis et al. [9] used an acidic  $\text{Fe(III)}_2(\text{SO}_4)_3$  solution as oxidizing agent at elevated temperatures to oxidize the metal sulfide (in his case copper- and zinc-sulfide) to metal sulfate and elemental sulfur, but a complete conversion of the metal sulfide was not achieved. In the process presently under development the regeneration of the absorbent will be done by means of oxidation of the precipitated metal sulfide to metal oxide [2]. In order to prevent the contamination of the off gases of the oxidation step with components other than sulfur dioxide and water, metal sulfate salts will preferably be used as absorbent. Presented in this contribution are the results of the experiments conducted to investigate the absorption of  $\text{H}_2\text{S}$  in some selected metal sulfates.

## 2. Theory

Sulfides of most bivalent metal ions, e.g. zinc, copper, silver, lead, magnesium, nickel and tin are highly insoluble. Therefore aqueous solutions containing these metal ions can be used as washing liquid in a desulfurization process. The overall reaction between  $\text{H}_2\text{S}$  and a bivalent metal ion is given

Table 2  
Elementary reaction scheme for precipitation reactions of sulfide and carbonate

Equation	Reaction (stoichiometry)	Equilibrium expression
(2)	$\text{H}_2\text{S}_\text{G} \rightleftharpoons \text{H}_2\text{S}_\text{L}$	$m_{\text{H}_2\text{S}} = \frac{[\text{H}_2\text{S}_\text{L}]_i}{[\text{H}_2\text{S}_\text{G}]_i} = \left( \frac{[\text{H}_2\text{S}_\text{L}]}{[\text{H}_2\text{S}_\text{G}]} \right)_{\text{Equilibrium}}$
(3)	$\text{H}_2\text{S}_\text{L} + \text{H}_2\text{O} \rightleftharpoons \text{HS}^- + \text{H}_3\text{O}^+$	$K_{\text{a1H}_2\text{S}} = \frac{[\text{HS}^-][\text{H}_3\text{O}^+]}{[\text{H}_2\text{S}_\text{L}]}$
(4)	$\text{HS}^- + \text{H}_2\text{O} \rightleftharpoons \text{S}^{2-} + \text{H}_3\text{O}^+$	$K_{\text{a2H}_2\text{S}} = \frac{[\text{S}^{2-}][\text{H}_3\text{O}^+]}{[\text{HS}^-]}$
(5)	$\text{S}^{2-} + \text{Me}^{2+} \rightleftharpoons \text{MeS} \downarrow$	$K_{\text{sp}} = [\text{S}^{2-}][\text{Me}^{2+}]$
(6)	$\text{CO}_{2,\text{G}} \rightleftharpoons \text{CO}_{2,\text{L}}$	$m_{\text{CO}_2} = \frac{[\text{CO}_{2,\text{L}}]_i}{[\text{CO}_{2,\text{G}}]_i} = \left( \frac{[\text{CO}_{2,\text{L}}]}{[\text{CO}_{2,\text{G}}]} \right)_{\text{Equilibrium}}$
(7)	$\text{CO}_{2,\text{L}} + \text{H}_2\text{O} \rightleftharpoons \text{HCO}_3^- + \text{H}_3\text{O}^+$	$K_{\text{a1CO}_2} = \frac{[\text{HCO}_3^-][\text{H}_3\text{O}^+]}{[\text{CO}_{2,\text{L}}]}$
(8)	$\text{HCO}_3^- + \text{H}_2\text{O} \rightleftharpoons \text{CO}_3^{2-} + \text{H}_3\text{O}^+$	$K_{\text{a2CO}_2} = \frac{[\text{CO}_3^{2-}][\text{H}_3\text{O}^+]}{[\text{HCO}_3^-]}$
(9)	$\text{CO}_3^{2-} + \text{Me}^{2+} \rightleftharpoons \text{MeCO}_3 \downarrow$	$K_{\text{sp}} = [\text{CO}_3^{2-}][\text{Me}^{2+}]$

in Eq. (1). The absorption of  $\text{H}_2\text{S}$  in, and the subsequent reaction with a metal sulfate solution will take place in several elementary steps shown in Table 2. First  $\text{H}_2\text{S}$  will be transported from the gas phase and dissolve physically in the liquid phase (Eq. (2)). In most practical cases equilibrium exists at the G/L interface, and the ratio of gas and liquid concentrations can be expressed as a distribution coefficient  $m$  [10]. The distribution coefficient is a function of liquid composition and temperature only when the gas phase behaves ideally. The dissolved  $\text{H}_2\text{S}$  molecule can now act as a diprotic acid (Eqs. (3) and (4)<sup>1</sup>). If the solubility product of the metal sulfide is exceeded then solid metal sulfide can form (Eq. (5)). Another reaction that can possibly occur when  $\text{CO}_2$  is also present is the reaction between  $\text{CO}_2$  and the metal ion in the washing liquor. This unwanted side reaction takes place according to a scheme similar to the reaction scheme of the precipitation reaction between  $\text{H}_2\text{S}$  and the metal ion.  $\text{CO}_2$  is first physically dissolved in water (Eq. (6)), and the dissolved  $\text{CO}_2$  then dissociates stepwise into bicarbonate and carbonate (Eqs. (7) and (8)). Solid metal carbonate can then be formed according to the reaction given in Eq. (9). Whether this precipitation indeed occurs depends on the solubility product. The numerical value of the equilibrium constant of the bisulfide/sulfide equilibrium, as well as the equilibrium constant for the solubility products for the metal sulfides can be found in the work of Licht [11], who evaluated these constants critically. The numerical values for the other equilibrium constants and gas–liquid distribution coefficients can be found in literature [12–14]. An overview of the numerical value of the various equilibrium constants at a temperature of 298 K is given in Tables 3–5.

### 2.1. Application of the equilibrium model for the determination of an operating window assuring selective desulfurization for a 1 molar metal sulfate solution

This simple model can now be used to estimate the vapor pressure of  $\text{H}_2\text{S}$  or  $\text{CO}_2$  in equilibrium with the correspond-

Table 3

The solubility products (based on concentrations) of the carbonate, hydroxide and sulfide salts of the metal ions used in this study at a temperature of 298 K [11,21]

$\text{Me}^{n+}$	$X^{m-}$		
	$\text{CO}_3^{2-}$	$\text{OH}^-$	$\text{S}^{2-}$
$\text{Fe}^{2+}$	$3.1 \times 10^{-11}$ $\text{FeCO}_3$	$4.9 \times 10^{-17}$ $\text{Fe}(\text{OH})_2$	$1.0 \times 10^{-21}$ $\text{FeS}$
$\text{Zn}^{2+}$	$1.2 \times 10^{-10}$ $\text{ZnCO}_3$	$4.1 \times 10^{-17}$ $\text{Zn}(\text{OH})_2$	$3.2 \times 10^{-26}$ $\text{ZnS}$
$\text{Cu}^{2+}$	$6.0 \times 10^{-6}$ $\text{CuCO}_3$	$2.4 \times 10^{-13}$ $\text{Cu}(\text{OH})_2$	$5.0 \times 10^{-41}$ $\text{CuS}$

ing solid metal sulfide or metal carbonate at a given pH and metal sulfate concentrations using the equilibrium constants given in Tables 3–5. Since the concentrations of  $\text{H}_2\text{S}$  and  $\text{CO}_2$  present in the gas leaving the desulfurization unit are determined by the product specification, the model can also be used to determine if a scrubbing solution is a suitable reactant for a selective desulfurization process. In Figs. 1–3 the equilibrium vapor pressure of  $\text{H}_2\text{S}$  and  $\text{CO}_2$  is plotted against the pH for a 1 molar metal sulfate solution. For a given product gas specification, these figures can be used to determine the operating window (a pH region in which metal sulfide precipitation can, but metal carbonate cannot occur) for a selective  $\text{H}_2\text{S}$  removal. Usually the  $\text{H}_2\text{S}$  specification for the product gas will vary between 4 and 500 ppmv  $\text{H}_2\text{S}$ ,

Table 4

First and second dissociation constants of  $\text{CO}_2$  and  $\text{H}_2\text{S}$  in water at a temperature of 298 K [11,14]

Equilibrium	$\text{p}K_{\text{a}}$
$\text{H}_2\text{S}/\text{HS}^-$	7.05
$\text{HS}^-/\text{S}^{2-}$	17.3
$\text{CO}_2/\text{HCO}_3^-$	6.35
$\text{HCO}_3^-/\text{CO}_3^{2-}$	10.33

Table 5

Distribution coefficients of  $\text{CO}_2$  and  $\text{H}_2\text{S}$  at a temperature of 298 K [12,13]

Equilibrium	$m$
$[\text{H}_2\text{S}]_\text{L}/[\text{H}_2\text{S}]_\text{G}$	2.5
$[\text{CO}_2]_\text{L}/[\text{CO}_2]_\text{G}$	0.84

<sup>1</sup> Note that the current model assumes ideal behavior of the components.

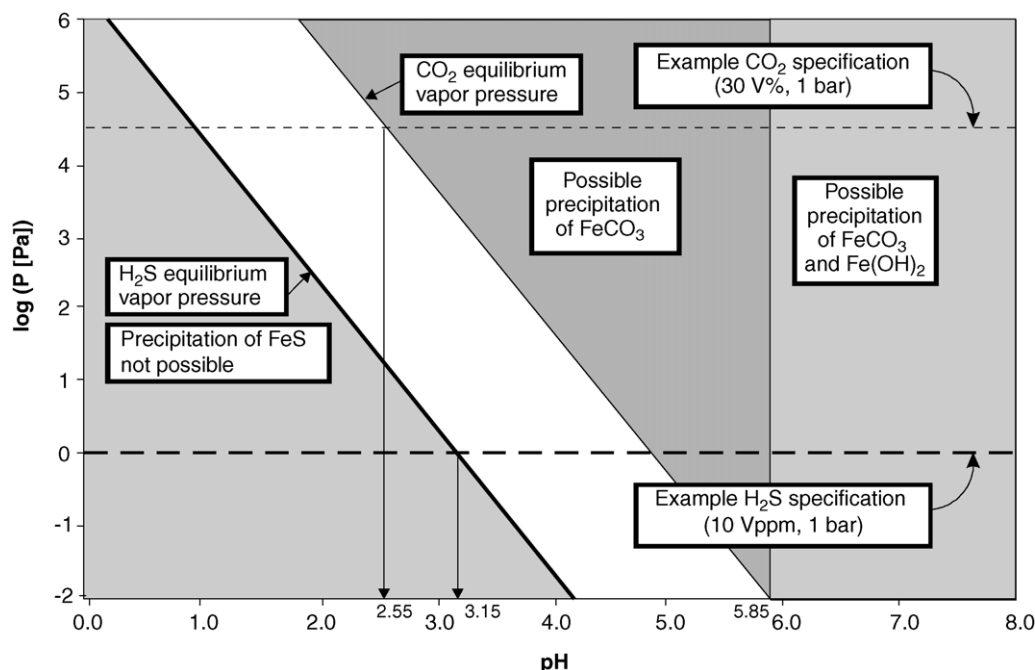


Fig. 1. Equilibrium vapor pressures of  $\text{CO}_2$  and  $\text{H}_2\text{S}$  as a function of pH for a 1 M  $\text{FeSO}_4$  solution at a temperature of 293 K. The dotted lines are the  $\text{H}_2\text{S}$  outlet specification (10 ppmv at 1 bara) and the  $\text{CO}_2$  vapor pressure in the inlet gas (30 vol.% at 1 bara).

depending upon further use. As an example a possible specification can be 10 ppmv  $\text{H}_2\text{S}$  and 30 vol.%  $\text{CO}_2$  at a pressure of 1 bara, which is typical specification for a biogas. This specification will be used in the following examples. In Figs. 1–3 not only the theoretically calculated equilibrium vapor pres-

ures, but also the currently specified vapor pressures of  $\text{H}_2\text{S}$  and  $\text{CO}_2$  are plotted as a function of the pH in case of a 1 molar  $\text{Fe(II)SO}_4$  (Fig. 1),  $\text{ZnSO}_4$  (Fig. 2) and a  $\text{CuSO}_4$  (Fig. 3) solution. The lines of the equilibrium pressure and gas phase specification intersect at the pH where precipita-

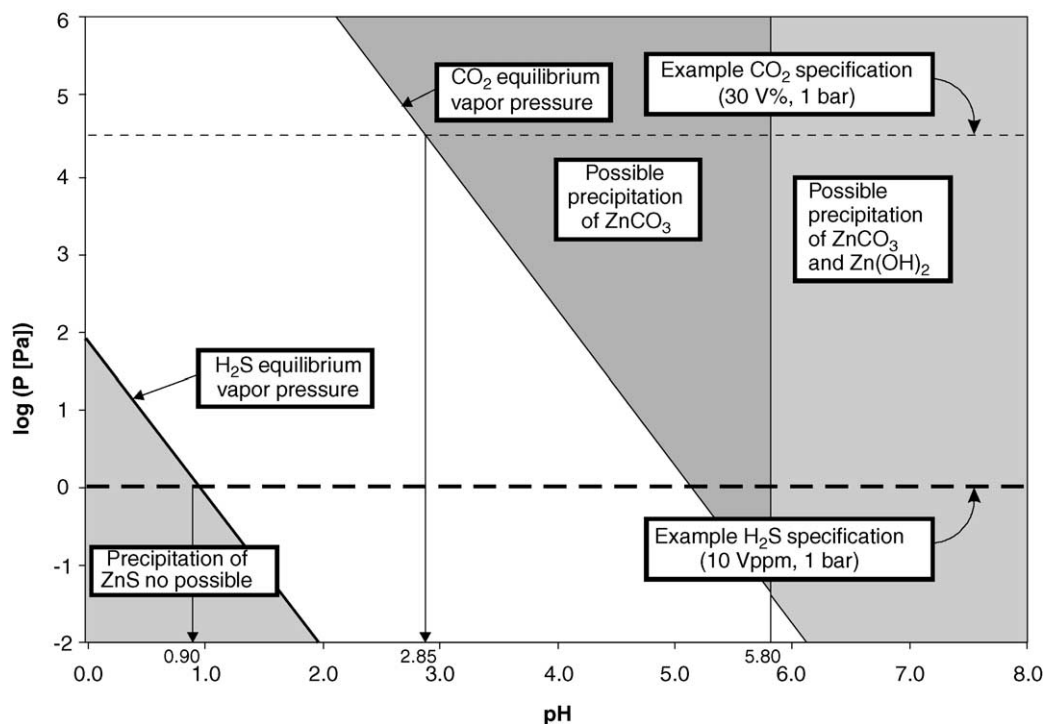


Fig. 2. Equilibrium vapor pressures of  $\text{CO}_2$  and  $\text{H}_2\text{S}$  as a function of pH for a 1 M  $\text{ZnSO}_4$  solution at a temperature of 293 K. The dotted lines are the  $\text{H}_2\text{S}$  outlet specification (10 ppmv at 1 bara) and the  $\text{CO}_2$  vapor pressure in the inlet gas (30 vol.% at 1 bara).

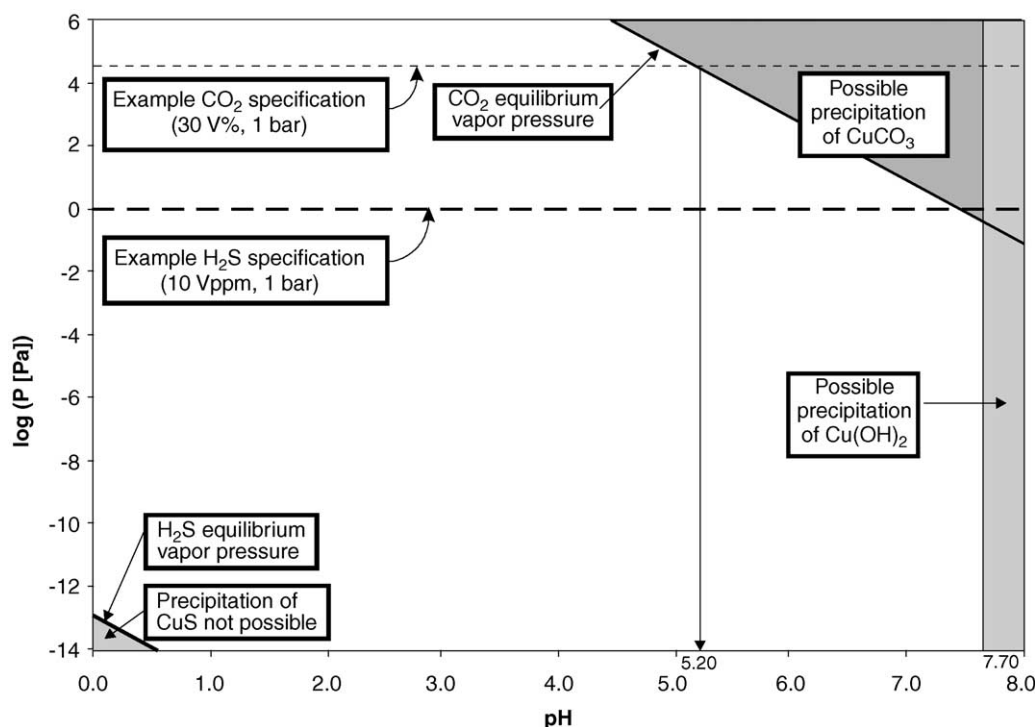


Fig. 3. Equilibrium vapor pressures of  $\text{CO}_2$  and  $\text{H}_2\text{S}$  as a function of pH for a 1 M  $\text{CuSO}_4$  solution at a temperature of 293 K. The dotted lines are the  $\text{H}_2\text{S}$  outlet specification (10 ppmv at 1 bara) and the  $\text{CO}_2$  vapor pressure in the inlet gas (30 vol.% at 1 bara).

tion can just take place. An overview of the pH values, above which precipitation can take place is given in Table 6. From this table it can be seen that, for the case of  $\text{Fe(II)SO}_4$ , the pH of the solution must not be higher than 5.85 to prevent the precipitation of iron hydroxide. Furthermore it can be seen that a pH of at least 3.15 is needed to meet the sulfur specification, while the precipitation of iron carbonate can already

take place at a pH of 2.55 and higher. This means that these theoretical calculations predict that it is not possible to remove  $\text{H}_2\text{S}$  down to 10 ppmv without removing  $\text{CO}_2$  if that component is present in a concentration of 30 vol.% at a total pressure of 1 bara. For a 1 molar  $\text{ZnSO}_4$  solution a pH of at least 0.90 is required to allow precipitation of zinc sulfide when the gas phase concentration of  $\text{H}_2\text{S}$  is just at the desired

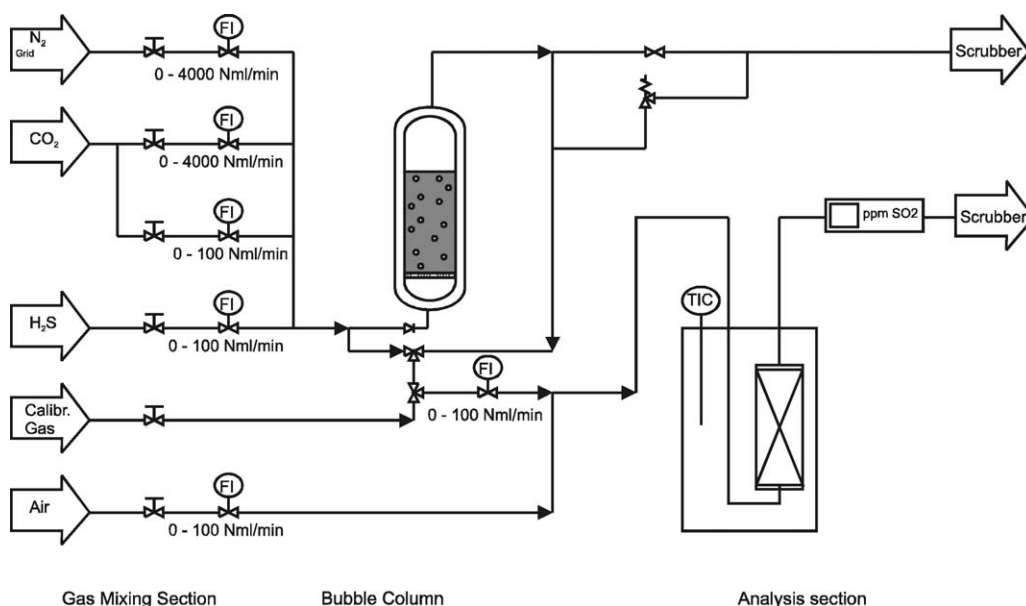


Fig. 4. Schematic representation of the experimental set-up.



Table 6

The minimum pH needed for precipitation when a 1 molar metal sulfate solution is brought in contact with a gas containing 10 ppmv H<sub>2</sub>S or 30 vol.% CO<sub>2</sub> at a pressure of 1 bara and a temperature of 298 K

Metal sulfate	pH needed for precipitation of		
	Metal sulfide	Metal carbonate	Metal hydroxide
FeSO <sub>4</sub>	3.15	2.55	5.85
ZnSO <sub>4</sub>	0.90	2.85	5.80
CuSO <sub>4</sub>	<0.00	5.20	7.70

specification. Fig. 2 shows that the precipitation of zinc carbonate may also take place. In this example, with 30 vol.% CO<sub>2</sub> at a pressure of 1 bara, the precipitation of zinc carbonate can take place at a pH of 2.85 and higher. Thus, theoretical calculations show that for a selective desulfurization down to 10 ppmv H<sub>2</sub>S without the co-precipitation of zinc carbonate the pH of the solution must be regulated between 0.90 and 2.85. Fig. 3 shows that the precipitation of copper sulfide can always occur if the pH is higher than 0 and the H<sub>2</sub>S vapor pressure is higher than 10<sup>-12</sup> Pa. From this figure it can also be seen that, with a gas phase composition of 30 vol.% CO<sub>2</sub> at a pressure of 1 bara, the precipitation of copper carbonate can take place at a pH of 5.20 and higher. This means that when using a CuSO<sub>4</sub> solution a very large operating window is obtained. For this theoretical example it is shown that as long as the pH is lower than 5.20 a selective removal of H<sub>2</sub>S is possible. These examples, which are given for 1 M metal sulfate solutions, show that for a selective H<sub>2</sub>S removal process in the presence of CO<sub>2</sub> the operating range increases in the order from Fe, Zn to Cu.<sup>2</sup>

### 3. Experimental

Absorption experiments have been carried out in a laboratory scale set-up schematically shown in Fig. 4. The set-up consists of three sections; a gas mixing section to prepare the desired gas mixture, a reactor section, and an analysis section. A more detailed drawing of the bubble column reactor, with a height of 62 cm and an inner diameter of 3 cm, is given in Fig. 5. During an experiment the bubble column was operated batch wise with respect to the liquid phase, and continuously with respect to the gas phase. The flow rate and composition of the gases were controlled using Brooks 5150 thermal mass flow controllers. A glass frit was used as bottom plate to create an even distribution of the bubbles in the reactor. To ensure isothermal operation of the bubble column a thermostatic bath (Tamson T 1000) was used to pump water with constant temperature through the annular space of the double walled reactor. The pH of the solution in the

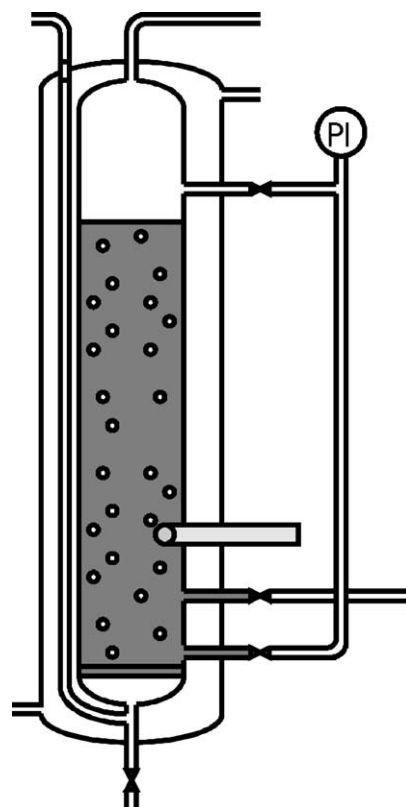


Fig. 5. Schematic representation of the reactor.

reactor was monitored by means of a Schott pH electrode. The pressure in the reactor was measured using a pressure gauge. The void fraction of the solution in the reactor could be determined by means of a gauge glass. Via small side openings the addition of e.g. anti-foaming agent or NaOH solution was possible if desired. The following experimental procedure was applied. The bubble column was filled with a freshly prepared metal sulfate solution. Then a small amount of NaOH solution (containing 10 mmol NaOH) was added to set the initial pH of the solution to the desired value and to generate a small amount of metal hydroxide. During the course of an experiment the pH will gradually decrease since hydronium ions are generated in the reaction; the metal hydroxide will act as a buffer and prevent a swift drop in pH immediately after the start of an experiment. When the metal sulfate solution in the reactor reached the desired temperature of 293 K, a gas with the desired composition was bubbled through the reactor at a superficial gas velocity of 0.02 m s<sup>-1</sup>. The pressure in the reactor was kept at 1.1 bara. A continuous gas sample flow was drawn from the reactor effluent stream. The H<sub>2</sub>S content of this stream was determined by mixing the sample stream with air and converting the H<sub>2</sub>S present in the sample stream to sulfur dioxide over stainless steel wool at 350 °C [15]. A MAIHAK UNOR 610 IR sulfur dioxide analyzer was used to determine the concentration of sulfur dioxide and therewith, indirectly, the concentration of H<sub>2</sub>S. During the experiments the concentration of SO<sub>2</sub> that left the reactor and the pH of the solution were recorded. The time

<sup>2</sup> It should be noted that for differently concentrated metal sulfate solutions, the same method can be applied to determine an operating window. However, for all equally concentrated solutions the width of the operating window will increase in the same (Fe, Zn to Cu) order as found for 1 M solutions.

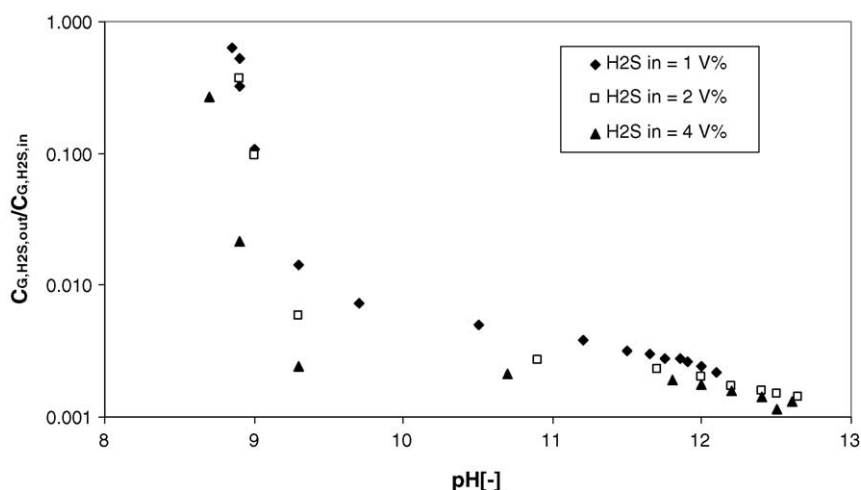


Fig. 6. The absorption of  $\text{H}_2\text{S}$  in a NaOH solution at superficial gas velocity of  $0.02 \text{ m s}^{-1}$  and a liquid column height of 0.265 m at a temperature of 293 K, and a pressure of 1.1 bara.

required to reach a new steady state concentration of  $\text{SO}_2$  after a sudden change in  $\text{H}_2\text{S}$  concentration in the gas stream entering the reactor was less than 1.5 min. The  $\text{Fe(II)SO}_4$ ,  $\text{ZnSO}_4$  and  $\text{CuSO}_4$  used were of analytical grade and were obtained from Across Chimica.  $\text{N}_2$  and  $\text{CO}_2$  were obtained from Hoek Loos, and had a purity of at least 99.9%.  $\text{H}_2\text{S}$  was obtained from Hoek Loos and had a purity of 99.0%. The calibration gas was prepared by Scott Specialty Gasses, and had a composition of 1.0 vol.%  $\text{H}_2\text{S} \pm 0.05\%$ . The air used for oxidation of the gas stream used for analysis was synthetic air and was obtained from Hoek Loos (21 vol.%  $\text{O}_2$ ). The method of analysis was checked using a mixture of the  $\text{H}_2\text{S}$  calibration gas and air in a known ratio. The  $\text{H}_2\text{S}$  in this calibration mixture was converted to sulfur dioxide over a catalyst at  $350^\circ\text{C}$  and the resulting mixture was then sent to the IR analyzer. The deviation between the measured concentration and the expected concentration was typically smaller than 2.5%.

## 4. Results and discussion

### 4.1. Characterization of the bubble column with an aqueous NaOH solution

To characterize the bubble column some experiments were performed using the absorption of  $\text{H}_2\text{S}$  in an aqueous 0.1 molar NaOH solution. That system was chosen because the reaction of  $\text{H}_2\text{S}$  and a NaOH solution is instantaneous with respect to mass transfer and the absorption of  $\text{H}_2\text{S}$  is therefore gas phase mass transfer controlled if the concentration of the NaOH concentration is sufficiently high [16]. The experimental data are presented in Fig. 6. From Fig. 6 it can be seen that, at a pH higher than 11, the conversion of  $\text{H}_2\text{S}$  was more or less independent of the pH and the initial concentration of  $\text{H}_2\text{S}$  in the gas. When the pH dropped below 9.5 the removal efficiency decreased significantly. The gas phase mass transfer coefficient ( $k_G a$ ) can then be determined

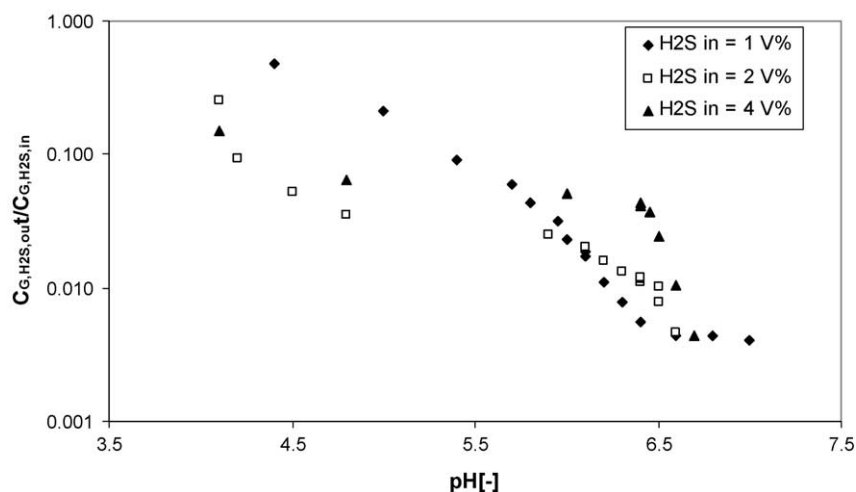


Fig. 7. The absorption of  $\text{H}_2\text{S}$  in a 1.0 M  $\text{Fe(II)SO}_4$  solution at a superficial gas velocity of  $0.02 \text{ m s}^{-1}$  and a column height of 0.495 m at a temperature of 293 K, and a pressure of 1.1 bara.



at high pH values with Eq. (10) (analogous to [10, p. 367]):

$$k_{Ga} = -\ln \left[ \frac{C_{out}}{C_{in}} \right] \frac{v_{sup,G}}{h} \quad (10)$$

For the NaOH/H<sub>2</sub>S system,  $k_{Ga}$  was determined to be approximately  $0.5 \text{ s}^{-1}$  in the present set-up. It should be mentioned that this value could not be determined more accurately since the concentration of H<sub>2</sub>S in the gas leaving the reactor is very low (At a  $C_{in,H_2S}$  of 1 vol.%,  $C_{out,H_2S}$  was approximately 20–80 ppmv) and therefore the concentration of SO<sub>2</sub> in the gas entering the analyzer was near the lower limit of the operating range of the analyzer. Therefore a small deviation in the measured concentration of H<sub>2</sub>S in the gas leaving the reactor value causes a large deviation in the determined value for  $k_{Ga}$ .

#### 4.2. The absorption of H<sub>2</sub>S in an aqueous solution of Fe(II)SO<sub>4</sub>

The absorption of H<sub>2</sub>S in aqueous 1 molar Fe(II)SO<sub>4</sub> solutions has been studied as a function of the pH of the solution and the concentration of H<sub>2</sub>S in the gas entering the reactor. At the start of an experiment the pH was brought to a value of approximately 7 by adding some NaOH. At a pH of approximately 4 the H<sub>2</sub>S uptake of the solution decreased significantly and a small amount of NaOH was added to bring the pH of the solution back to its original value. Then a gas stream with a different concentration of H<sub>2</sub>S was brought in contact with the solution and the experiment was repeated. Using this procedure the concentration of H<sub>2</sub>S in the gas entering the reactor was varied between 1 and 4 vol.%. During the entire experiment the conversion with respect to the metal ions was less than 8%, and thus the assumption that the concentration of metal ions did not change significantly during the experiment is justified. The experimental data are presented in Fig. 7. From the experimental results obtained with an Fe(II)SO<sub>4</sub> solution it can be concluded that it is possible to remove more than 99% of the H<sub>2</sub>S from a gas stream that initially contains in between 1 and 4 vol.% H<sub>2</sub>S when the pH of the solution is higher than 6.7. With the pH above 6.7 the conversion of H<sub>2</sub>S appeared to be somewhat lower than the conversion of H<sub>2</sub>S when using NaOH with a pH above 11, although a longer liquid column was used. This might be caused by a change in specific contact area in the reactor in case the process is still gas phase mass transfer controlled. However, another (more likely) cause of the lower conversion may be that the absorption of H<sub>2</sub>S was not (completely) gas phase mass transfer limited, but also partly influenced by precipitation kinetics and/or liquid phase mass transfer. At a pH lower than approximately 5 the experimentally determined conversion of H<sub>2</sub>S drops considerably. The results of the equilibrium calculations, given in Table 7, however, show that a virtually complete desulfurization should be possible at pH values as low as 3. Since the bulk concentration of Fe<sup>2+</sup> ions has not dropped significantly due to the precipitation reaction, the most probable cause for this discrepancy is

Table 7

Comparison of the experimental results and the results of the theoretical calculations regarding the absorption of H<sub>2</sub>S in an aqueous 1 M solution of FeSO<sub>4</sub> for a  $C_{G,H_2S,in}$  of 1 vol.%

pH	$C_{G,H_2S,out}/C_{G,H_2S,in}$	Theoretical prediction	
		Experimental results (Fig. 7)	Equilibrium calculations
		Gas phase mass transport limited absorption <sup>a</sup>	
6.7	0.004	$4.2 \times 10^{-6}$	$7.9 \times 10^{-11}$
6	0.023	$4.2 \times 10^{-6}$	$2.0 \times 10^{-9}$
5	0.21	$4.2 \times 10^{-6}$	$2.0 \times 10^{-7}$
4	0.5	$4.2 \times 10^{-6}$	$2.0 \times 10^{-5}$
3	–	$4.2 \times 10^{-6}$	$2.0 \times 10^{-3}$
2	–	$4.2 \times 10^{-6}$	$2.0 \times 10^{-1}$
1	–	$4.2 \times 10^{-6}$	–

The lower detection limit of the equipment does not allow measurements below a value of 20 ppmv H<sub>2</sub>S, thus the lowest possible experimentally determined value for  $C_{G,H_2S,out}/C_{G,H_2S,in}$  was 0.002.

<sup>a</sup> Based on experimental conditions as specified in Section 4.2 and a  $k_{Ga}$  value of  $0.5 \text{ s}^{-1}$ .

that the rate of the precipitation reaction drops significantly long before the reacting system approaches equilibrium, an effect also reported by Nielsen [17] and Söhnle and Garside [18]. Thermodynamic equilibrium calculations show that at the pH values needed for an efficient H<sub>2</sub>S removal one cannot exclude the formation of solid iron(II) hydroxide or iron(II) carbonate (see Fig. 1 and Table 6). Even at lower pH values, where the scrubbing solution would be less efficient (and consequently a longer contact time would be required), the possible formation of iron carbonate cannot be excluded when CO<sub>2</sub> is present in the gas. Aqueous Fe(II)SO<sub>4</sub> solutions therefore do not seem very suited when a selective desulfurization process is required.

#### 4.3. The absorption of H<sub>2</sub>S in an aqueous solution of ZnSO<sub>4</sub>

For an aqueous ZnSO<sub>4</sub> solution the H<sub>2</sub>S conversion was also measured for various ingoing H<sub>2</sub>S concentrations and as a function of the pH of the solution. The experimental procedure was identical to the procedure in the experiments with FeSO<sub>4</sub> solutions. The pH of the solution immediately after the addition of NaOH was 5.8 (the precipitation of zinc hydroxide at that pH prohibits a higher pH value). At a pH of approximately 2.5 the H<sub>2</sub>S conversion became lower than 75% and the experiment was stopped. A number of experiments was performed with superficial gas velocities varying between  $0.02$  and  $0.04 \text{ m s}^{-1}$  and with H<sub>2</sub>S concentrations in the gas entering the reactor varying between 1 and 4 vol.%. The experimental data are presented in Fig. 8. When the experimental results are compared, it can be seen that aqueous ZnSO<sub>4</sub> and Fe(II)SO<sub>4</sub> solutions behave similarly with respect to the absorption of H<sub>2</sub>S. Again the experimental maximum conversion of H<sub>2</sub>S was slightly lower than the conversion observed when using a NaOH solution with a pH above 11, although a longer liquid column was used. When the absorp-

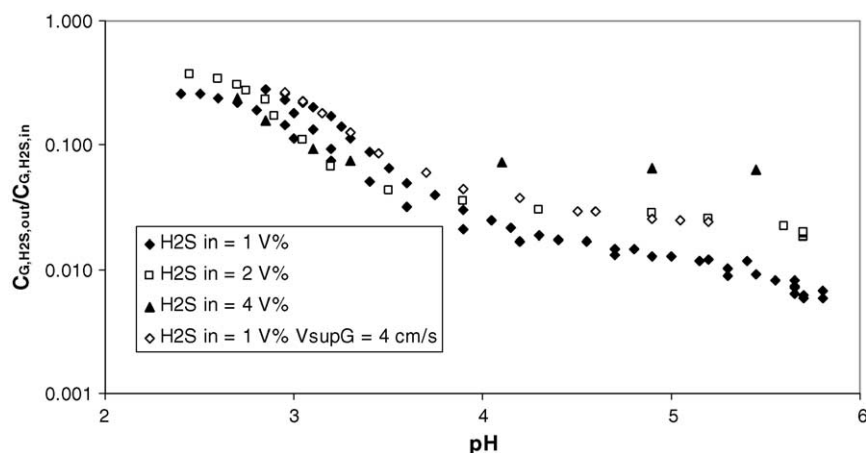


Fig. 8. The absorption of  $\text{H}_2\text{S}$  in a 1.0 M  $\text{ZnSO}_4$  solution at a superficial gas velocity of 0.02 and 0.04  $\text{m s}^{-1}$  and a liquid height of 0.495 m at a temperature of 293 K, and a pressure of 1.1 bara.

tion of  $\text{H}_2\text{S}$  in a  $\text{ZnSO}_4$  solution is compared to the absorption of  $\text{H}_2\text{S}$  in an  $\text{Fe(II)SO}_4$  solution, a noticeable difference is that when using a  $\text{ZnSO}_4$  solution a high conversion of  $\text{H}_2\text{S}$  can also be achieved at pH values below 6. It appeared for example to be possible to remove more than 99% of  $\text{H}_2\text{S}$  from a gas stream that initially contained 1 vol.%  $\text{H}_2\text{S}$  at a pH value of 5. To see a substantial decrease in  $\text{H}_2\text{S}$  conversion, the pH had to drop below a value of 4. Equilibrium calculations however, show that for the conditions applied a near complete removal of  $\text{H}_2\text{S}$  should be possible at pH values as low as 0.90 (see also Fig. 2 and Table 8). A possible explanation for the difference between the experimentally determined and the maximum theoretical conversion could be the aforementioned decrease in the rate of the precipitation reaction. The experimental results in Fig. 8 show that, in order to maintain a high  $\text{H}_2\text{S}$  conversion when using a  $\text{ZnSO}_4$  solution in the experimental set-up, the pH of the washing liquor must be kept at a value of 5 or higher. From Fig. 2 it can be seen that at a pH of 5 the formation of solid zinc carbonate is already possible at  $\text{CO}_2$  vapor pressures as low as 1.6 Pa. Therefore the precip-

Table 8

Comparison of the experimental results and the results of the theoretical calculations regarding the absorption of  $\text{H}_2\text{S}$  in an aqueous 1 M solution of  $\text{ZnSO}_4$  for a  $C_{G,\text{H}_2\text{S},\text{in}}$  of 1 vol.%

pH	$C_{G,\text{H}_2\text{S},\text{out}}/C_{G,\text{H}_2\text{S},\text{in}}$	Theoretical prediction	
		Experimental results (Fig. 8)	Equilibrium calculations
			Gas phase mass transport limited absorption <sup>a</sup>
7	–		$4.2 \times 10^{-6}$
5.7	0.006		$4.2 \times 10^{-6}$
5	0.01		$4.2 \times 10^{-6}$
4	0.02		$4.2 \times 10^{-6}$
3	0.18		$4.2 \times 10^{-6}$
2	–		$4.2 \times 10^{-6}$
1	–		$4.2 \times 10^{-6}$
0	–		$4.2 \times 10^{-6}$

The lower detection limit of the equipment does not allow measurements below a value of 20 ppmv  $\text{H}_2\text{S}$ , thus the lowest possible experimentally determined value for  $C_{G,\text{H}_2\text{S},\text{out}}/C_{G,\text{H}_2\text{S},\text{in}}$  was 0.002.

<sup>a</sup> Based on experimental conditions as specified in section 4.3 and a  $k_{GA}$  value of  $0.5 \text{ s}^{-1}$ .

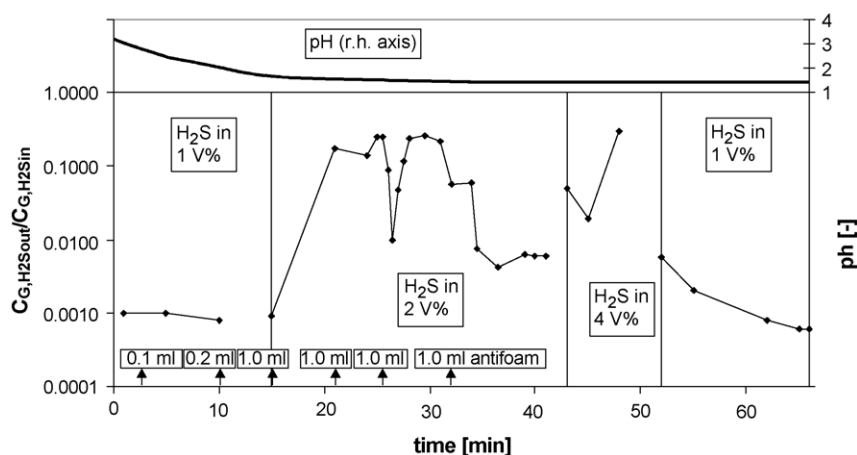


Fig. 9. The absorption of  $\text{H}_2\text{S}$  in a 1.0 M  $\text{CuSO}_4$  solution at a superficial gas velocity of 0.02  $\text{m s}^{-1}$  and a liquid height in the column of 0.265 m at a temperature of 293 K, and a pressure of 1.1 bara.

itation of  $\text{ZnCO}_3$  that can occur when  $\text{CO}_2$  is present in the gas stream that has to be desulfurized can only be excluded when the column is operated at lower pH values, where a high  $\text{H}_2\text{S}$  conversion might only be possible at the cost of a much longer contact time, and thus much larger equipment size. The equilibrium diagram given in Fig. 2 therefore only seems suitable to establish an operating window to assure a selective desulfurization using a  $\text{ZnSO}_4$  solution, but does not tell everything about the width of the operating window for an efficient  $\text{H}_2\text{S}$  removal process.

#### 4.4. The absorption of $\text{H}_2\text{S}$ in an aqueous solution of $\text{CuSO}_4$

Since copper sulfide has an extremely low solubility product, it is expected that a  $\text{CuSO}_4$  solution will have the best desulfurization performance of the three metal sulfate solutions studied. A  $\text{H}_2\text{S}$  absorption experiment using a 1 molar  $\text{CuSO}_4$  solution was carried out to verify this. Since  $\text{H}_2\text{S}$  conversions of more than 99% could be achieved during the

entire experiment, no NaOH was added to the solution during the entire experiment. The initial pH of the  $\text{CuSO}_4$  solution was 3.2. During the experiment the amount of  $\text{H}_2\text{S}$  in the gas entering the reactor was varied between 1 and 4 vol.%. The experimental results are presented in Fig. 9.

##### 4.4.1. Absorption of $\text{H}_2\text{S}$ from a gas containing 1 vol.% $\text{H}_2\text{S}$ in a $\text{CuSO}_4$ solution

During two periods of the experiment (from the start of the experiment until  $t = 15$  min, and from  $t = 52$  to  $t = 66$  min) the concentration of  $\text{H}_2\text{S}$  in the inlet gas was 1 vol.%. From Fig. 9 it can be seen that a conversion of  $\text{H}_2\text{S}$  of more than 99.5% could be reached during these periods. The pH of the solution decreased from 3.2 to 2.1 during the first period, and remained constant at a value of 1.4 during the second period. During the experiment the solid copper sulfide formed appeared to induce foaming in the bubble column. An anti-foaming agent (a silicon oil/water emulsion) was added to the solution to reduce the extent of foaming and to improve the column performance. Small amounts of anti-foaming agent

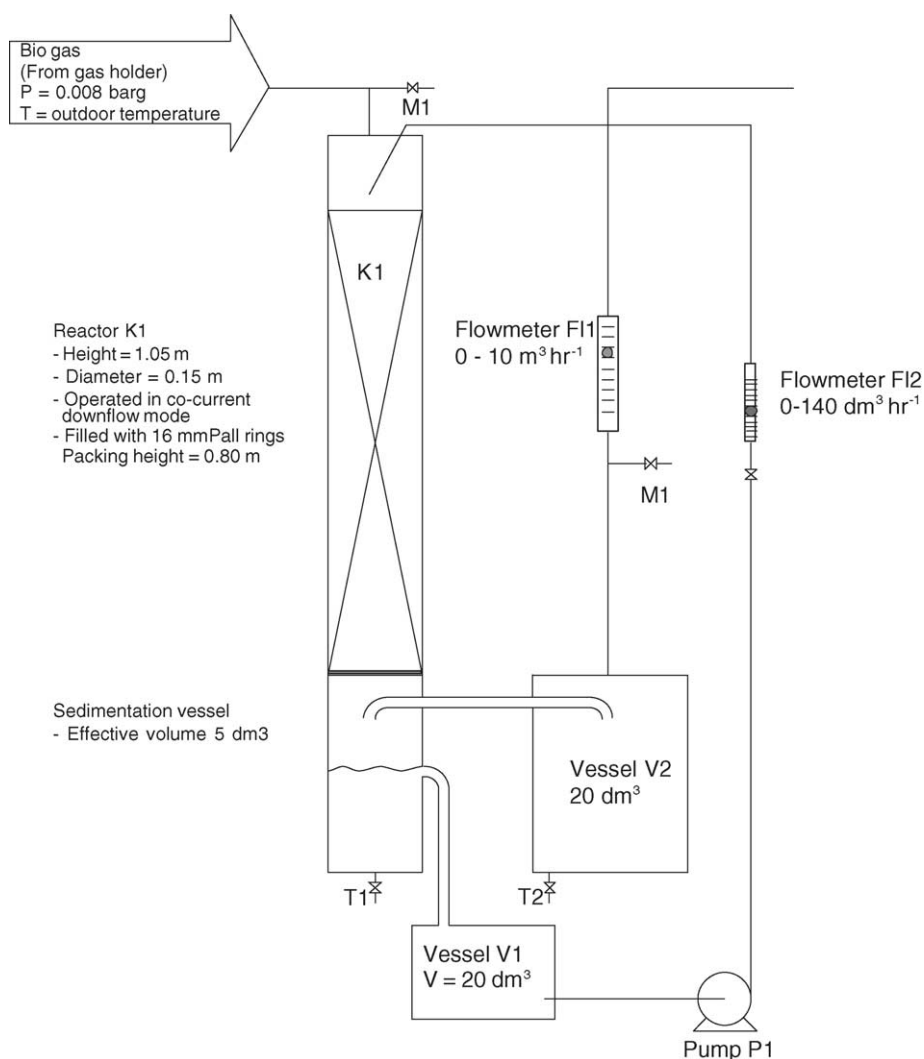


Fig. 10. Schematical representation of the experimental set-up.

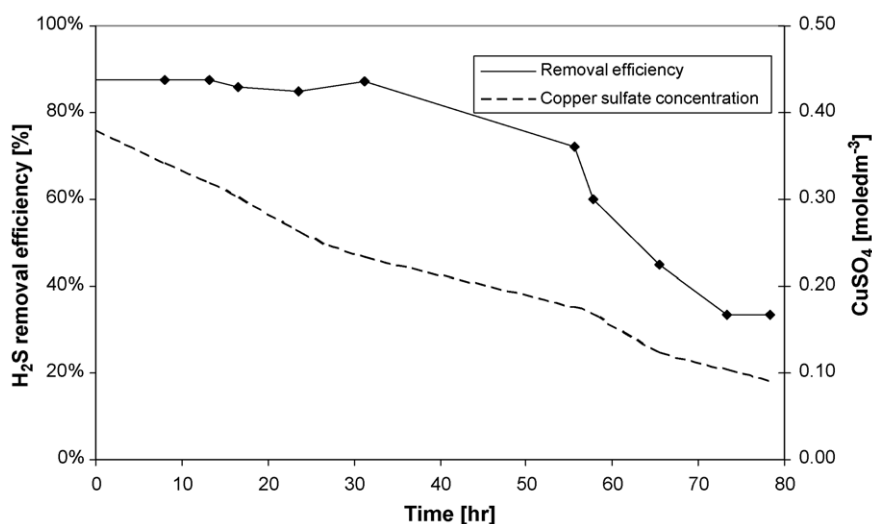


Fig. 11. H<sub>2</sub>S conversion as a function of time during experiment 1,  $T = -5$  to  $9^\circ\text{C}$ ,  $P = 1$  atm  $[\text{CuSO}_4]_{\text{initial}} = 0.37$  M,  $[\text{H}_2\text{S}]_{\text{in}} = 500\text{--}2000$  ppm.

were added to the CuSO<sub>4</sub> solution during the initial 15 min of the experiment, see also Fig. 9. When precautions taken to prevent foaming are effective, like e.g. during the first 10 min of the experiment of which the results are shown in Fig. 9, the observed conversion appeared to be similar to the conversion of H<sub>2</sub>S when using a 0.1 M NaOH solution. In both cases ultimately approximately 99.9% of the H<sub>2</sub>S present in a gas stream containing 1 vol.% H<sub>2</sub>S was removed. During the second period of the experiment in which the concentration of H<sub>2</sub>S in the inlet gas was 1 vol.% (from  $t = 52$  to  $t = 66$  min), the conversion of H<sub>2</sub>S increased gradually from 99.5 to 99.9%. This H<sub>2</sub>S concentration in the outlet gas however is too close to the lower detection limit of the set-up to allow for a conclusion with respect to the observed variation in H<sub>2</sub>S concentration.

#### 4.4.2. Absorption of H<sub>2</sub>S from a gas containing 2 vol.% H<sub>2</sub>S in a CuSO<sub>4</sub> solution

When a gas containing 2 vol.% H<sub>2</sub>S was fed to the reactor the extent of foaming increased, therefore, larger amounts of antifoaming agent were added to the solution; 1 ml of antifoaming agent was added after 15, 21, 25 and 31 min while 4 ml of anti-foaming agent was added after 32 min. The results presented in Fig. 9 show that the H<sub>2</sub>S conversion varies between approximately 75 and 90% when the foaming phenomena is insufficiently suppressed (in the time frame from 15 to 32 min). However, more than 99% conversion of H<sub>2</sub>S can be achieved if sufficient anti-foaming agent is added to the washing solution (from  $t = 32$  to  $t = 41$  min). The maximum observed conversion of H<sub>2</sub>S is somewhat lower than the conversion when 1 vol.% of H<sub>2</sub>S was present in the gas entering the bubble column, but this effect can probably be ascribed to a change in the specific contact area in the reactor, or a slightly different gas flow pattern caused by the presence of solids near the gas/liquid interface.

#### 4.4.3. Absorption of H<sub>2</sub>S from a gas containing 4 vol.% H<sub>2</sub>S in a CuSO<sub>4</sub> solution

Due to foaming of the solution in the bubble column it was not possible to realize stable operation at a H<sub>2</sub>S concentration of 4 vol.% (from  $t = 43$  to  $t = 52$  min). In this situation the observed conversion of H<sub>2</sub>S dropped significantly, but this most probably has to be attributed to precipitation related foaming phenomena.

#### 4.4.4. General conclusions regarding the absorption of H<sub>2</sub>S from a gas stream in an aqueous solution of CuSO<sub>4</sub>

The results of the experiments carried out in a bubble column using a 1 M CuSO<sub>4</sub> solution show that the H<sub>2</sub>S conversion can be similar to the conversion of H<sub>2</sub>S when using a 0.1 M NaOH solution at similar column length. In both the CuSO<sub>4</sub> and the NaOH case approximately 99.8% of the H<sub>2</sub>S present in a gas stream containing 1 vol.% H<sub>2</sub>S could be removed. No restrictions were found with respect to a lower limit of the pH during the experiment (the pH value of the solution varied between 3.2 and 1.4 during the experiment). It also appeared that the H<sub>2</sub>S removal efficiency of the bubble column decreased significantly with increasing H<sub>2</sub>S concentration in the inlet gas. It is likely that the cause for this must be found in foaming related changes in the hydrodynamic behavior of the column. From the results of the thermodynamical equilibrium calculations shown in Fig. 3, and the experimental results it can be concluded that a relatively large operating window to assure a selective desulfurization using a CuSO<sub>4</sub> solution can be defined: to avoid the precipitation of CuCO<sub>3</sub> at a CO<sub>2</sub> vapor pressure of 0.3 bara (30 vol.% at 1 bara) the pH of the solution must be kept below 5.20, while experiments show that the scrubbing solution still works effectively at pH values as low as 1.4.

## 5. Pilot plant scale experiments: the absorption of H<sub>2</sub>S from a biogas stream

### 5.1. Introduction

To demonstrate the absorption of H<sub>2</sub>S from an industrial gas in a CuSO<sub>4</sub> solution on a larger scale a pilot plant was constructed. In this pilot plant an industrial biogas stream, containing a range of components besides H<sub>2</sub>S, was brought in contact with a CuSO<sub>4</sub> solution. The feasibility of the re-use of a regenerated copper sulfate solution was also investigated in a separate experimental series.

### 5.2. Experimental set-up and procedure

The pilot plant (see Fig. 10) can be subdivided in the reactor section and the liquid circulation circuit.

#### 5.2.1. Reactor section and gas circuit

From an industrial biogas holder, in which biogas is stored at a pressure of 0.008 barg and at ambient temperature, a gas stream was withdrawn. The bio-gas stream consisted of a mixture of CO<sub>2</sub> (approximately 35 vol.%) and CH<sub>4</sub> (approximately 65 vol.%) with a H<sub>2</sub>S content varying from 350 to 2000 ppmv. The biogas was led through the reactor (K1) (i.d. 0.15 m), which was operated in co-current down flow mode. In the reactor a random packing, consisting of polypropylene 16 mm Pall rings was dumped. The height of the packing was 0.8 m. A liquid distributor was used to ensure an optimal division of the CuSO<sub>4</sub> solution over the packing. The co-current down flow packed bed contactor was chosen because it is suited for a fast reaction, has a low pressure drop, and allows for a high gas phase reactant conversion [19]. In the reactor the CuSO<sub>4</sub> solution reacts with H<sub>2</sub>S present in the biogas. The desulfurized gas that leaves the absorber was led through vessel V2 and a gas flow meter (F11). To prevent the possible carry-over of foam that might have formed in the biogas scrubber a gas–liquid separator (V2) was installed in the gas outlet.

#### 5.2.2. Liquid circulation circuit

The CuSO<sub>4</sub> solution was stored in vessel V1. The centrifugal pump P1 was used to transport the CuSO<sub>4</sub> solution from vessel V1 via flow meter F12 to the packed bed reactor (K1). After the slurry left the reactor, it flowed into a vessel under the reactor, designed to separate the solid particles from the solution. An overflow on the separator vessel allowed the washing liquor to flow back to vessel V1. The settled particles could, together with a certain amount of washing liquid, be removed from the set-up through valve T1.

#### 5.2.3. Experimental procedure

To ensure adequate supervision, the pilot plant was operated during day shift hours only. During the weekend the biogas producing facility was not operated, and hence the

pilot plant was also not operated. The following experimental procedure was applied. Vessel V1 was filled with 20 dm<sup>3</sup> of a CuSO<sub>4</sub> solution. When the ambient temperature was below the freezing point some anti-freeze (ethylene glycol) was added to the washing liquid. The washing liquid was pumped through the liquid circulation circuit at a fixed flow rate. Once the liquid circulation was operational the biogas was fed to the pilot plant. During operation the concentration of H<sub>2</sub>S of the gas entering and leaving the reactor was monitored daily. The experiment was terminated when the degree of H<sub>2</sub>S removal decreased considerably.

### 5.3. Results

Two long-term experiments have been carried out with the pilot plant set-up. First goal was to show that the proposed desulfurization process is suitable to realize a high degree of H<sub>2</sub>S removal (see Section 5.3.1). Secondly, the effect of the re-use of a regenerated copper sulfate solution on the absorption characteristics was investigated (see Section 5.3.2).

#### 5.3.1. Experimental series 1 in the pilot plant

A total of 20 dm<sup>3</sup> of an aqueous 0.5 M CuSO<sub>4</sub> solution was brought in vessel V1. Since the ambient temperature varied between −5 and 9 °C, 5 dm<sup>3</sup> of anti-freeze (ethylene glycol) was added to the washing liquid, resulting in a mixture of 25 dm<sup>3</sup> 0.37 M CuSO<sub>4</sub>. The gas stream through the column was set at approximately 3 m<sup>3</sup> h<sup>−1</sup> and the flow of the washing liquid was approximately 0.14 m<sup>3</sup> h<sup>−1</sup>. During operation the concentration of H<sub>2</sub>S of the gas entering and leaving the reactor was monitored daily (see Fig. 11). From this figure it can be seen that when the CuSO<sub>4</sub> concentration in the washing liquid is sufficiently high, the scrubber is capable of decreasing the H<sub>2</sub>S concentration in the gas with approximately 85%. The average concentration of H<sub>2</sub>S in the gas stream leaving the absorber was approximately 170 ppm. This removal efficiency may seem somewhat lower than might be expected based on the removal efficiency of the lab scale bubble column experiments, but the relatively small wetted fraction of the packing explains for this observation as will be demonstrated via calculations of which the results are shown in Table 9. The CuSO<sub>4</sub> concentration is also plotted in Fig. 11 as a function of time.<sup>3</sup> When the CuSO<sub>4</sub> concentration decreased to approximately 0.17 mol dm<sup>−3</sup> (at a pH value of approximately 0.60), the degree of removal dropped substantially. It is not likely that the lower copper ion concentration is responsible for this effect. However, since a steadily increasing concentration of (hydrophobic) CuS particles is present in

<sup>3</sup> The course of the copper sulfate concentration in time has been estimated from the total absorbed amount of H<sub>2</sub>S. The initial and final copper concentration of the washing liquid have been determined analytically however. The difference between the two approaches appeared to be less than 20%, which seems quite acceptable taking into consideration that e.g. the H<sub>2</sub>S concentration in the biogas varies during the day and was not monitored continuously.



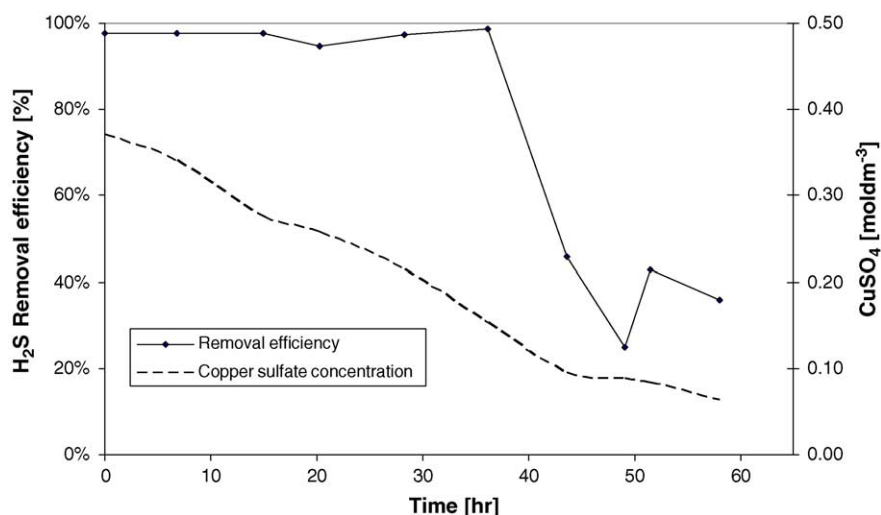


Fig. 12.  $\text{H}_2\text{S}$  conversion as a function of time during experiment 2.  $P = 1 \text{ atm}$ ,  $[\text{CuSO}_4]_{\text{initial}} = 0.375 \text{ M}$ ,  $[\text{H}_2\text{S}]_{\text{in}} = 350\text{--}1000 \text{ ppm}$ .

the circulating liquid (as was visually observed) the foaming phenomenon (also observed during the lab scale bubble column experiments) might be held responsible for the decrease in  $\text{H}_2\text{S}$  removal efficiency. In Table 9 the characteristics of the absorption column are listed together with the mass transfer

parameters of that column calculated using the well-known relations given by Onda et al. [20]. It appears that the experimentally obtained degree of  $\text{H}_2\text{S}$  removal (85% removal) agrees quite well with the theoretical degree of  $\text{H}_2\text{S}$  removal expected in case of a totally gas phase mass transfer limited  $\text{H}_2\text{S}$  absorption (79% removal).

Table 9

Absorption column characteristics and calculated performance based on a gas phase mass transfer limited process

Parameter	Experiment 1	Experiment 2
<b>Column</b>		
Diameter (m)	0.15	0.15
Height packing (m)	0.8	0.8
Temperature ( $^{\circ}\text{C}$ )	−5 to 9	5–12
Pressure (Pa)	$10^5$	$10^5$
<b>Packing</b>		
Type	Pall rings	Pall rings
Diameter (m)	$16 \times 10^{-3}$	$16 \times 10^{-3}$
Specific surface area ( $\text{m}^2 \text{m}^{-3}$ )	340	340
<b>Absorbent slow</b>		
Mass flow liquid ( $\text{kg s}^{-1}$ )	0.039	0.28
Copper concentration ( $\text{mol m}^{-3}$ )	170–370	90–370
Liquid loading ( $\text{kg m}^{-2} \text{s}^{-1}$ )	2.2	15.8
Hydrodynamic regime	Trickling flow	Trickling flow
<b>Gas flow</b>		
Gas volume flow ( $\text{m}^3 \text{s}^{-1}$ )	$8.3 \times 10^{-4}$	$11.5 \times 10^{-4}$
Gas loading ( $\text{kg m}^{-2} \text{s}^{-1}$ )	0.031	0.042
Gas residence time (s)	22	16
<b>Mass transfer parameters</b>		
$k_L$ [20] ( $\text{m s}^{-1}$ )	$1.1 \times 10^{-4}$	$2.6 \times 10^{-4}$
$a_w$ [20] ( $\text{m}^2 \text{m}^{-3}$ )	46	93
$k_G$ [20] ( $\text{m s}^{-1}$ )	$2.0 \times 10^{-3}$	$2.4 \times 10^{-3}$
$k_{La}$ ( $\text{s}^{-1}$ )	$5.3 \times 10^{-3}$	$2.5 \times 10^{-2}$
$k_{Ga}$ ( $\text{s}^{-1}$ )	$9.0 \times 10^{-2}$	$2.3 \times 10^{-1}$
<b>Fraction of <math>\text{H}_2\text{S}</math> removed</b>		
Theoretical conversion in case of gas phase mass transfer limitation (Eq. (10))	0.79	0.96
Experimental value	0.85	0.985

### 5.3.2. Experimental series 2 in the pilot plant

The objective of this experiment was to demonstrate that  $\text{H}_2\text{S}$  can be efficiently removed from a biogas stream, on a pilot plant scale, using a regenerated  $\text{CuSO}_4$  solution. The spent solution from the previous experiment (Section 5.3.1) was regenerated and used in the subsequent experimental series. The following procedure was used to regenerate the solution. First the copper sulfide particles were separated from the spent solution and then the copper sulfide was oxidized to copper oxide (for the regeneration procedure see [2]). Finally the  $\text{CuSO}_4$  solution was regenerated by dissolving the obtained copper oxide in the original (acidic) spent solution. A total amount of  $20 \text{ dm}^3$  of an aqueous  $\text{CuSO}_4$  solution (0.37 M) was brought in vessel V1. The temperature of the set-up was equal to the outdoor temperature. During this experiment the gas stream through the column was approximately  $4 \text{ m}^3 \text{h}^{-1}$ , and to maximize the wetted fraction of the packing (as a learning experience of the results from the previous experiment) the flow of the washing liquid was increased to approximately  $1.0 \text{ m}^3 \text{h}^{-1}$ . During operation the concentration of  $\text{H}_2\text{S}$  of the gas entering and leaving the reactor was monitored daily. When the  $\text{CuSO}_4$  concentration in the washing liquid was above approximately  $0.15 \text{ mol dm}^{-3}$ , the scrubber was capable of decreasing the  $\text{H}_2\text{S}$  concentration in the gas with approximately 98.5%. This is quite close to the theoretically predicted conversion of 96% given in Table 9 for a gas phase mass transfer limited process. When the  $\text{CuSO}_4$  concentration of the circulating liquid decreased until approximately  $0.15 \text{ mol dm}^{-3}$  (at a pH value of approximately 0.60), as in the previous experiment, the degree of removal



dropped considerably. The exact reason for this behavior is unknown, but it can probably be ascribed to the appearance of foaming in the column caused by the increasing concentration of CuS particles in the circulating liquid (Fig. 12).<sup>4</sup> As a consequence of the high liquid circulation rate the solid particles did not settle completely in vessel V1 (this was observed visually). However, the solids in the slurry (at the end of the experiment the slurry contained approximately 3 wt.% of solids) did not cause any notable problems with respect to plugging of the packed bed. The experimental results show that the removal of H<sub>2</sub>S on a pilot plant scale can take place very efficiently. The concentration of H<sub>2</sub>S in the biogas that leaves the scrubber is comparable to the concentration of H<sub>2</sub>S in the biogas leaving the reactor in case of a gas phase mass transfer limited absorption process (see Table 9). Furthermore, it is shown that use of regenerated copper sulfate solution does lead to removal efficiencies as expected based on a gas phase mass transfer limited process.

## 6. Conclusions

The desulfurization of gas streams using aqueous Fe(II)SO<sub>4</sub>, ZnSO<sub>4</sub> and CuSO<sub>4</sub> solutions as washing liquor has been studied theoretically and experimentally. A thermodynamic study has been used to determine a theoretical operating window for selective desulfurization, with respect to the pH of the scrubbing solution, in which the metal sulfate solution can react with H<sub>2</sub>S, but not with CO<sub>2</sub> in the gas or hydroxide from the solution. The theoretical operating window increases in the order of iron, zinc to copper.

Experimental verification in a lab scale bubble column showed that when a 1 molar Fe(II)SO<sub>4</sub> solution was used as washing liquor the degree of acidity in the bubble column appeared to have a pronounced influence on the desulfurization performance. Equilibrium calculations show that at the experimentally required pH the precipitation of iron carbonates is hard to prevent when CO<sub>2</sub> is also present in the gas that has to be desulfurized. This makes it unlikely that an aqueous Fe(II)SO<sub>4</sub> solution is a suitable absorbent when a selective desulfurization process is required.

The experimental results show that, although the operating window becomes larger, an aqueous ZnSO<sub>4</sub> solution behaves similarly with respect to the absorption of H<sub>2</sub>S as an FeSO<sub>4</sub> solution. Equilibrium calculations show that the formation of solid zinc carbonate can be avoided for a typical biogas composition. Therefore an aqueous ZnSO<sub>4</sub> solution shows

some promise for a selective desulfurization process as long as the pH of the solution is regulated within certain boundaries ( $2 < \text{pH} < 2.85$  for a typical biogas composition).

A high H<sub>2</sub>S conversion could be obtained down to a pH of 1.4 (lowest pH tested) when a 1M CuSO<sub>4</sub> solution was used as absorbent. The experimentally observed H<sub>2</sub>S conversion when using a concentration of 1 vol.% H<sub>2</sub>S in the inlet stream appeared to be similar to the conversion of H<sub>2</sub>S when using a 0.1 M NaOH solution, indicating that in this case the absorption was gas phase mass transfer controlled. Unfortunately during the experiments the copper sulfide precipitate caused foaming problems in the column; the extent of foaming increased with an increasing percentage H<sub>2</sub>S in the gas stream entering the column. Addition of an anti-foaming agent reduced these problems to a certain extent. Since thermodynamic calculations show that the formation of solid copper hydroxide is only possible at a pH above 7.70, an acidic or unbuffered CuSO<sub>4</sub> solution is a suitable solvent for the proposed desulfurization process. Selective desulfurization is only possible when the co-precipitation of copper carbonate is avoided. The exact value of the pH at which this precipitation occurs depends on the partial pressure of CO<sub>2</sub> in the contaminated gas stream: at a pH value of 5.2 the theoretical maximum allowable CO<sub>2</sub> partial pressure using a 1 M CuSO<sub>4</sub> solution is 30,000 Pa (30% at 1 bar).

To demonstrate the potential of the desulfurization process additional desulfurization experiments have been carried out on a pilot plant scale using an industrial biogas stream. The pilot plant was a co-current operated packed bed reactor in which fresh and regenerated CuSO<sub>4</sub> solutions were used. The experimental results show that the removal of H<sub>2</sub>S from biogas takes place very efficiently and is, at the applied conditions, probably dictated by gas phase mass transfer limitations. No problems with respect to plugging of the random packing by the precipitate were encountered. However, it is likely that for long operation times foaming in the packed column did occur.

From the thermodynamic study and the results obtained from the pilot plant and laboratory scale absorber, it can be concluded that when using a CuSO<sub>4</sub> solution this new desulfurization process is able to remove H<sub>2</sub>S from gas streams selectively with respect to CO<sub>2</sub>. The observed high conversion of H<sub>2</sub>S over a wide operating window makes the further development of a selective desulfurization process based on the use of aqueous CuSO<sub>4</sub>, and possibly ZnSO<sub>4</sub> solutions very attractive.

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<sup>4</sup> After the experiment was terminated a relatively large amount (7 dm<sup>3</sup>) of liquid was found in the overflow vessel. The copper concentration of that liquid was found to be 0.20 mol dm<sup>-3</sup>. The copper concentration demonstrates that at least a significant fraction of that liquid must have entered the overflow vessel in the time frame before the decrease in removal efficiency occurred (see Fig. 12). The most likely mechanism that causes the carry-over of the washing liquid to the overflow vessel is foaming. This indicates that prior to the sudden decrease in removal efficiency, at least some degree of foaming took place.

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